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COLUMBIA UNIVERSITY

**JOINT SERVICES ELECTRONICS PROGRAM
FINAL REPORT**

**RESEARCH INVESTIGATION DIRECTED TOWARD EXTENDING
THE USEFUL RANGE OF THE ELECTROMAGNETIC SPECTRUM**

for Grant DAAG55-97-1-0166

For the Period May 1, 1997 – April 30, 2001

Presented to:

THE JOINT SERVICES TECHNICAL COORDINATING COMMITTEE

Representing: THE U.S. ARMY RESEARCH OFFICE,

THE OFFICE OF NAVAL RESEARCH,

and THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Submitted by:

COLUMBIA RADIATION LABORATORY

DEPARTMENTS OF APPLIED PHYSICS, CHEMISTRY,

ELECTRICAL ENGINEERING, PHYSICS

COLUMBIA UNIVERSITY in the City of New York

NEW YORK, NEW YORK 10027

June 30, 2001

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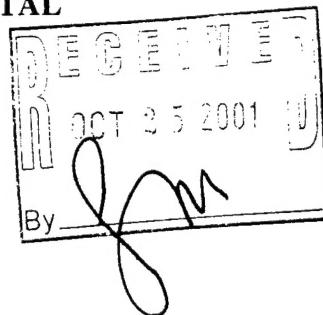
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MICROELECTRONIC SCIENCES LABORATORIES

2001 OCT 24 PM 3:00

MEMORANDUM OF TRANSMITTAL

October 12, 2001

U.S. Army Research Office
Attention: Sylvia Hall
AMSRL-RO-BI
4300 South Miami Boulevard
Durham, NC 27703-9142



RE: COLUMBIA UNIVERSITY'S JSEP FINAL REPORT
CONTRACT DAAG55-97-1-0166 for the period May 1, 1997 – April 30, 2001

Dear Mrs. Hall:

An extra copy of Columbia University's Final JSEP Report is enclosed as requested by William Clark, Associate Director, Electronics Division, for Contract: DAAG55-97-1-0166 for the period May 1, 1997 – April 30, 2001. Original copies of this report were sent to ARO the last week of June 2001. An extra copy is also being sent as requested to AMSRL-RO-EL (Mr. William Clark).

Title: Research Investigation Directed Toward Extending the Useful Range of the Electromagnetic Spectrum

Thank you for your support.

Please let Columbia's Office of Projects and Grants know if you have further questions (Veronica Murray at (212) 854-6851).

Sincerely,

Melvin Ziegel for George Flynn
JSEP Laboratory Director

bb
cc: JSEP file

Joint Services Electronics Program Final Report
for Contract DAAG55-97-1-0166
Covering the period May 1, 1997 – April 30, 2001

**“Research Investigation Directed Toward Extending the Useful Range
of the Electromagnetic Spectrum”**

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data gathering

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1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	6/30/01	Final Report, 5/97-4/2001 15 Apr 97 - 14 Apr 01	
4. TITLE AND SUBTITLE Joint Services Electronics Program Final Report: Research Investigation Directed Toward Extending the Useful Range of the Electromagnetic Spectrum			5. FUNDING NUMBERS DAAG55-97-1-0166
6. AUTHORS George W. Flynn, Richard M. Osgood, Jr., Louis E. Brus, Tony F. Heinz and Irving P. Herman			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Trustees of Columbia University in the City of NY Columbia University, Columbia Radiation Laboratory 530 West 120 th St., Room 1001, Mail Code 8903 New York, NY 10027			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			1. SPONSORING / MONITORING AGENCY REPORT NUMBER DAAG55-97-1-0166 36376.31-BL-JSE
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See page 4			
14. SUBJECT TERMS See page 5.			15. NUMBER OF PAGES 42
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.
Prescribed by ANSI Std.
298-102

20011113 111

ABSTRACT (Standard Form 298 No. 13)

Experiments are described that have the goal of understanding the basic physics of quantum confined electronics. In the first experiment new fabrication processes for making GaSb-based quantum dots have been examined. The scientific goal of this work is to develop methods to realize damage free etching of the dots. In the second experiment stepped metal surfaces have been used to measure the scattering cross-sections of electrons at simple features, such as used in quantum corrals.

Mesoscopic science has been investigated in several areas using local probe and confocal optical methodologies: (1) The self-assembly properties of metallic and semiconductor nanocrystals, and the collective electrical and optical properties that result from self-assembly, were explored on graphite. The observed patterns show that the particles behave as phase separating 2D van der Waals particles. (2) Electric Force Microscopy was developed to detect the presence of a single charge on a single nanocrystal in a thin film at 23 C. This EFM method was also used to explore the electrostatic properties of self-assembled Trioctyl phosphine oxide layers on graphite. (3) The Raman scattering of single Rhodamine 6G molecules at junctions between large Ag particles was detected with high signal to noise ratio. This work has been extended to nanocrystal dimers coupled by rigid linker molecules. (4) Carbon nanotubes are probably the most novel electronic material system that has been discovered in the past decade. Optical methods were developed to obtain the Raman spectra of single tubes. It was observed that an interference occurs between vibrational and electronic scattering, creating a Fano lineshape in the Resonance Raman Spectra.

Current mode-locked laser technology can provide time resolution as fast as $10 \text{ fs} = 10^{-14} \text{ s}$. These capabilities have had a major impact on many areas of science and advanced technology. Methods have been examined in which this extraordinary capability could be exploited to generate and detect electrical fields on transmission lines and in other circuit geometries with a time resolution dictated by the laser pulse duration. These efforts are motivated by both technological considerations (characterization of high-speed electronic and optoelectronic devices) and by scientific considerations (time-domain far-infrared spectroscopy and materials characterization). This work resulted in the demonstration of a new non-contact method of electric field generation involving optical rectification and in a new detection scheme suitable for Si and other centrosymmetric materials that relies on the process of optical second-harmonic generation.

A basic study of long-chain organic molecules that represent a model system for those used in organic molecular devices or in polymer thin films has been performed. The studies use STM techniques to probe and control order in thin films, specifically those formed at the liquid-solid interface. The molecular arrangement of adsorbates at the liquid-solid interface is, furthermore, very important in the study of wetting, lubrication, adhesion, adsorption and the fabrication of future microelectronic devices. These studies have also been extended to systems incorporating chiral molecules. Determining and controlling the chirality of molecules that form monolayer films on surfaces represents an important step in the development of molecular devices. Ultimately, it should be possible to construct highly uniform films of

molecules having only a single chiral species. Such films can be of enormous importance as sensors and optical discriminators in many device applications.

The preparation and properties of porous SiC (PSC) films prepared by electrochemical anodization from 6H SiC were studied in a series of experiments that included: photoluminescence and Raman scattering of PSC, reflectance to determine the effective-medium dielectric function of PSC films, and successful SiC vapor-phase epitaxy on PSC substrates as monitored by polarized micro-Raman scattering. The structural phase transitions and ferroelectric ordering in crystalline bulk and thin film relaxor lead zinc niobate - lead titanate (PZN-PT) were studied from -190°C to 600°C using polarized micro-Raman scattering. The optical and structural properties of several large-band gap materials were studied, including δ -doped ZnSe:Te, $Zn_{1-x}Be_xSe$ and GaN. Little evidence for interdot coupling of carriers was seen in three-dimensional arrays of organically passivated CdSe nanocrystals under hydrostatic pressure, probed by photoluminescence and absorption spectroscopies. Using FTIR ATR to study arrays of CdSe nanocrystals capped with pyridine, it was shown that only about 30% of the pyridine ligands remain after three days of drying.

SUBJECT TERMS (Standard Form 298 No. 14)

- ab initio* calculations
- adsorbates
- alcohols
- alkane
- amine
- arrays
- Atomic Force Microscopy (AFM)
- Bi-FET
- bromide
- carbon nanotubes
- CdSe
- charge transfer salts
- chemical assisted ion etching
- chemical etching
- chirality
- chloride
- coherence properties
- coherent surface effects
- copper surface
- cutoff frequency
- dielectric
- dielectric function
- disulfide
- electron cyclotron resonance (ECR) etching
- enhanced tunneling current
- entangled photons
- epilayers
- femtosecond measurements
- fractal exponent estimation
- functional group
- GaAs
- GaInP
- GaN
- GaSb
- GaSb-based materials
- graphite
- harmonic generation
- heat of adsorption
- heterojunction bipolar transistor
- high electron mobility transistor
- homodyne detection
- hydrocarbons
- hydrostatic pressure
- infrared semiconductor materials
- InGaN
- InP
- iodide
- Kronig-Penney model
- laser surface spectroscopy
- lateral confinement
- localization
- luminescence
- maximum oscillation frequency
- multiquantum well (MQW)
- nanocrystals
- nonclassical light
- nonlinear optics
- one-dimensional quantum confinement
- optical rectification
- orientation
- parametric downconversion
- phonons
- photoemission
- photoluminescence
- photonic band gap
- photonic crystals
- porous layers
- pulse generation
- quantum dots
- quantum wells
- Raman
- Scanning Tunneling Microscopy (STM)
- second-harmonic generation
- self-assembly
- semiconductor nanocrystal
- SiC
- silicon ion insulator
- solid/liquid interface
- stepped surface
- strained layers
- structure
- superlattice
- surface photoabsorption
- thiols
- Ti:Sapphire
- two photon photoemission
- ultrafast optoelectronics
- vapor phase epitaxy
- VPE

BASIC RESEARCH ON THE ELECTROMAGNETIC SPECTRUM

1. QUANTUM CONFINEMENT IN ELECTRONIC AND MAGNETIC MATERIALS

1.1 Nanoscale Fabrication For Advanced Semiconductor Devices (Mid IR Lasers and Photonic Crystals)

Richard M. Osgood, Jr., Principal Investigator
Research Area 1, Work Unit 1

(212) 854-4462

1.1A High-quality Etched Quantum Structures in GaSb-based Material

GaSb-based compound semiconductors are of increasing importance because of a wide range of emerging optoelectronic applications at mid-infrared wavelengths. For example, lasers with GaInAsSb active layers and AlGaAsSb confining layers can provide good optical and electrical confinement and are able to produce high power at low-threshold current densities [1]. Thermophotovoltaic cells with high internal quantum efficiency and high open-circuit voltage have been achieved with GaInAsSb[2]. For devices made of GaSb and its alloys, it is often desirable to replace wet chemical etching with dry etching because of the more anisotropic profile, uniformity and reproducibility of the latter. Despite the technological importance of GaSb-based ternary and quaternary materials, investigation of the dry etching of these materials has been limited. For example, electron cyclotron resonance (ECR) plasma etching, which is known to be suitable for III-V materials because of its high etch rate at low ion energy and pressure[3], has not been extensively studied for etching of GaSb-based ternary and quaternary alloys. Here, electron cyclotron resonance plasma etching with a mixture of argon and chlorine has been used to fabricate submicrometer-scale GaInAsSb/AlGaAsSb multiple-quantum-well (MQW) structures.

In our study, the gas-composition dependence and temperature dependence of the etch rate was determined. As shown in the inset of Fig.1, smooth surfaces with vertical sidewalls were obtained at chlorine concentrations between 15% and 28% and a substrate temperature of 150°C. To characterize any MQW damage for the etching conditions, the etched features were examined with photoluminescence spectroscopy with the 647 nm line of a Kr⁺ ion laser. The data obtained from the luminescence study were analyzed with a mathematical model[4] that assumes that the nonradiative damaged surface layer is thin compared to the bulk volume of the material. The results suggest that our ECR etching conditions introduce little, if any, bulk and near-surface damage; see Fig.1. This work was done in close collaboration with George Turner and his group at MIT-Lincoln Laboratory.

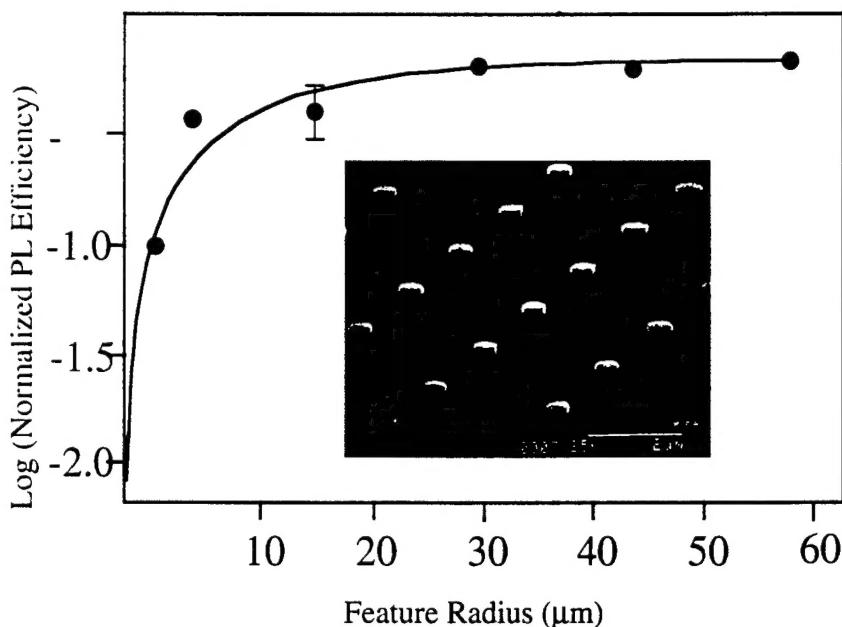


Fig 1. Luminescence efficiency as a function of the etched feature size. The solid line is the model described in Ref. 5. The inset shows a scanning electron micrograph of the etched features.

1.1B Fundamental Physics of Electron Motion at Interfaces: Observation of One-Dimensional Physics on Nanotextured Surfaces

(X. J. Shen, H. Kwak, D. Mocuta, A. M. Radojevic, S. Smadici, R. M. Osgood, Jr.)

We have used high-resolution, angle-resolved two-photon photoemission to observe a new one-dimensional surface state, 0.27 eV below the Fermi level, on a stepped model surface. This new surface state was observed on the periodic $14\text{\AA} \times 2\text{\AA}$ steps on Cu(775). The surface was investigated to determine if any evidence of reduced dimensionality is present in its electronic structure. The experiments used high-resolution, angle-resolved, two-photon photoemission (AR2PPE) in conjunction with a high-repetition-rate femtosecond optical source to examine the dispersion and energy distribution curves of this surface state on the stepped surface. Comparative dispersion measurements along and perpendicular to the step edges showed that one of these surface states was occupied and had a one-dimensional character; this state apparently results from step-potential confinement. The surface of the single-crystal sample was probed under a variety of surface conditions. While this state is quenched at large values of oxygen exposure, the state appears to be enhanced by a small coverage of O_2 . Further studies such as systematic time-resolved measurements on the newly observed state, STM observations of clean and oxygen exposed Cu(775) surface, step decoration with model adsorbates such as Xe, and, finally, polarization-dependence experiments may lead to new insights into the localization physics. The experiments on this system have been discussed in more detail in the Physical Review article cited in the publications.

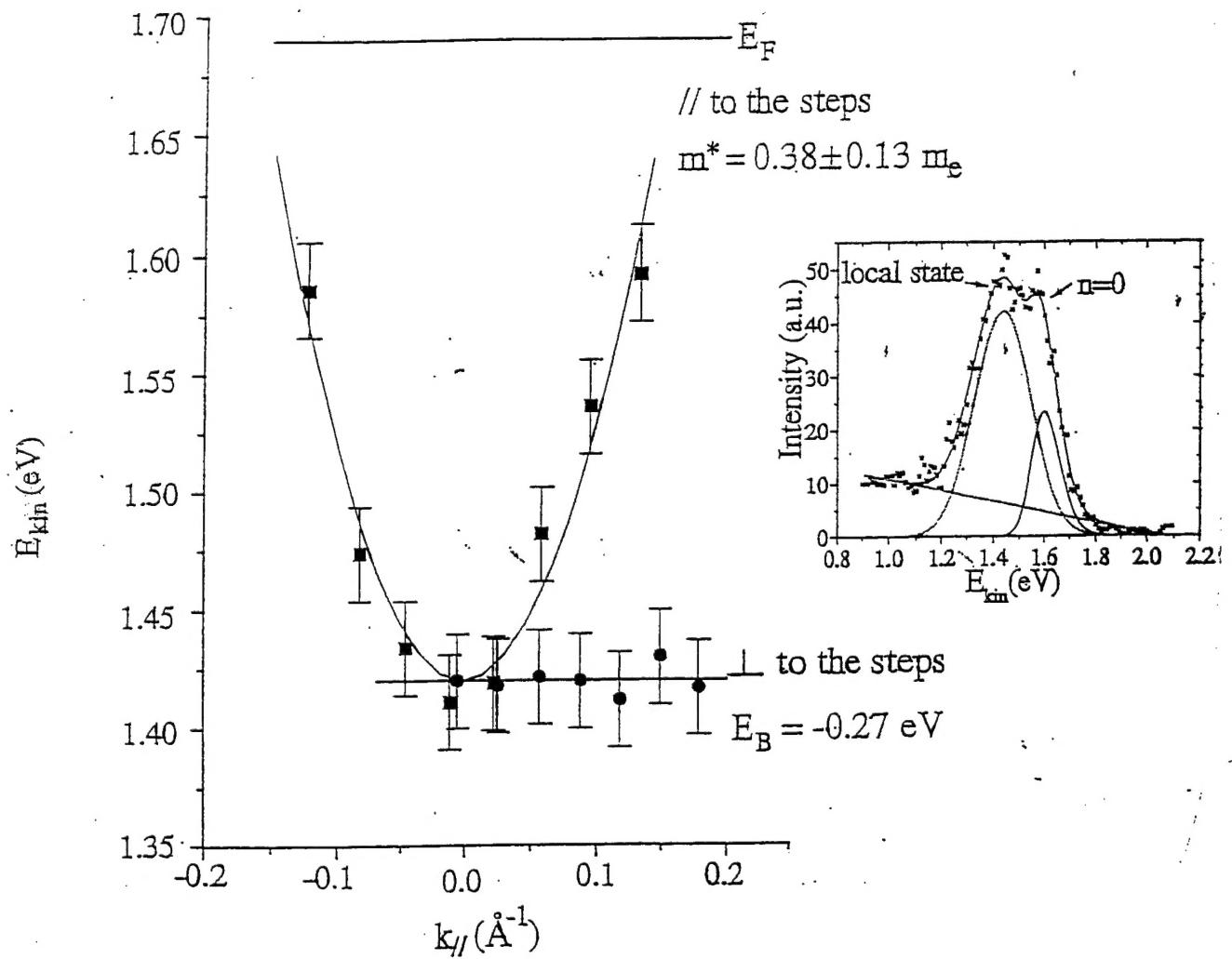


Fig. 2. Dispersion of the newly observed occupied band perpendicular and parallel to the step. Monochromatic 2PPE at 3.1 eV is used. The inset provides one typical electron distribution curve, taken at $\theta=9$ degrees which shows the co-existence of both the localized state and the $n=0$ surface state.

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- [1] G. W. Turner, H. K. Choi, D. R. Calawa, J. V. Pantano, and J. W. Chludzinski, *J. Vac. Sci. Technol. B* **12** (2), 1266-8 (1994).
- [2] H. K. Choi, C. A. Wang, G. W. Turner, M. J. Manfra, D. L. Spears, G. W. Charache, L. R. Danielson, and D. M. Depoy, *Appl. Phys. Lett.* **71**, 3758 (1997).
- [3] S. J. Ren, F. Pearton, and C. R. Abernathy, *Appl. Phys. Lett.* **64**, 1673 (1994).
- [4] E. M. Clausen, Jr., H. G. Craghead, J. M. Worlock, J. P. Harbison, L. M. Schiavone, L. Florez, and B. van der Gaag, *Appl. Phys. Lett.* **55**, 1427 (1989).

JSEP PUBLICATIONS AND PRESENTATIONS of Professor Richard Osgood

1. Papers published in peer reviewed journals (1997-2001):

- X. Y. Wang, X. J. Shen and R. M. Osgood, Jr., "Surface Electron Motion Near Moatomic Steps: Two-Photon Photoemission Studies on Stepped Cu(111)," *Phys. Rev. B* 56, 7665 (1997).
- K. A. Khan, J. E. Moryl, D. A. Slater, P. J. Lasky, and R. M. Osgood, Jr., "Energy- and Angle-Resolved Photodynamics of Ethyl Bromide on GaAs(110)," *J. Chem. Phys.* 101, 9077 (1997).
- L.-L. Chao, G. S. Cargill III, M. Levy, R. M. Osgood, Jr. and G. F. McClane, "Cathodoluminescence Study of GaAs Quantum Wells and of Quantum Dots Fabricated by Magnetron Reactive Ion Etching," *Appl. Phys. Letts.* 70, 408 (1997).
- G. Nagy, R. U. Ahmad, M. Levy and R. M. Osgood, Jr., "Chemically Assisted Ion Beam Etching of Submicron Features in GaSb," *Appl. Phys. Lett.* 72, 1350 (1998).
- G. Nagy, M. Levy, R. Scarmozzino, R. M. Osgood, Jr., H. Dai, R. E. Smalley, C. A. Michaels, E. T. Sevy, G. W. Flynn and G. F. McLane, "Carbon Nanotube Tipped Atomic Force Microscopy for Measurement of <100 nm Etch Morphology on Semiconductors," *Appl. Phys. Lett.* 73, 529 (1998).
- R. M. Osgood, Jr. and X. Wang, "Image States on Single-Crystal Metal Surface," Chapter in *Solid State Physics*, H. Ehrenreich and F. Spaepen, eds., page 1, Vol. 51, Academic Press (1998).
- X. J. Shen, H. Kwak, D. Mocuta, A. Radojevic, S. Smadici, and R. M. Osgood, Jr., "Observation of a One-Dimensional State on Stepped Cu(775)," *Phys. Rev. B* 163, 165403-165410 (2000).

2. Papers published in non-peer-reviewed journals or in conference proceedings:

None

(c) Papers presented at meetings, but not published in conference proceedings

- M. Osgood, Jr., "The Role of Energy Partitioning and Surface Reconstruction in Photoinitiated Electron Attachment to Oriented Alkyl Bromides Adsorbed on GaAs," with N. Camillone III, K. Khan, J. E. Moryl, and J. Yarmoff, 58th Annual Physical Electronic Conference, Penn State University, University Park, PA, June 14 - 17, 1998. R. M. Osgood, Jr., "The Role of Energy Partitioning and Surface Reconstruction in Photoinitiated Electron Attachment to Oriented Alkyl Bromides Adsorbed on GaAs," with N. Camillone III, K. Khan, J. E. Moryl, and J. Yarmoff, 58th Annual Physical Electronics Conference, Penn State University, University Park, PA, June 14-17, 1998.
- R. M. Osgood, Jr., "Chemically Assisted Ion-Beam Etching of Submicrometer Features in GaSb-based Quantum Wells," with G. Nagy, R.U. Ahmad, M. Levy, M. J. Manfra, and G.W. Turner, American Vacuum Society Meeting, Baltimore Convention Center, Baltimore, MD, November 2- 6, 1998.
- R. M. Osgood, Jr., "Observation of Non-dispersive States on Stepped Cu(111)," with H. Kwak, X. J. Shen, and A. M. Radojevic, CLEO/QELS '99 Baltimore Convention Center, Baltimore, MD, May 23 - 28, 1999.
- R. M. Osgood, Jr., "Momentum-Dependent Ultrafast Dynamics of Image States on Flat and Stepped Cu(111) Surfaces," with X. J. Shen, H. Kwak, and A. M. Radojevic, CLEO/QELS '99, Baltimore Convention Center, Baltimore, MD, May 23 - 28, 1999.
- R. M. Osgood, Jr., "K-dependence of Image State Lifetime Measurements on Cu(111) Surface with Time-resolved and Angle-resolved Photoemission," with H. Kwak, A. M. Radojevic, and X. J. Shen, The American Physical Society, Atlanta, GA, March 20 - 26, 1999.
- R. M. Osgood, Jr., "Two-Photon Photoemission Study of Stepped Cu(111) Surface Using Femtosecond Laser Pulses," with X. J. Shen, H. Kwak, and A. M. Radojevic, The American Physical Society,

Atlanta, GA, March 20 - 26, 1999.

R. M. Osgood, Jr., "Image State Electrons: A Model System for Electron Transfer at Surfaces," (invited talk), University of Sherbrooke, Montreal Canada, May 4, 1999.

R. M. Osgood, Jr., "Optical Manipulation of Surface Electrons: Chemical Reactions and Quantum Structures," OSA ILS/XV Symposium, Symposium on Lasers at Surfaces, Santa Clara, CA, September 26-October 2, 1999.

R. M. Osgood, Jr., "Optical Manipulation of Surface Electrons: Reactions and Nanostructures," Brookhaven National Laboratory, Upton, New York, November 5, 1999.

R.M. Osgood, Jr. "Slicing Dielectric Crystals with Ions: New Materials for Electronic and Optoelectronic Integration," Materials Science Seminar, University of Wisconsin, Madison, WI, November 18, 1999.

Richard Osgood Jr., Miguel Levy, and J. Fujita, "Progress in Integrated Optical Isolators," OSA IPR 2000, Quebec City, Canada, July 12-14, 2000.

R.M. Osgood, Jr., K. Adib, N. Camillone, J.P. Fitts, D. Mocuta, K.T. Rim, G.W. Flynn, and S.A. Joyce, "Thermal Production of Phossgene from Carbon Tetrachloride Reactions on Natural Single Crystal - Fe203 Surfaces in Ultrahigh Vacuum," 47th American Vacuum Society Meeting, Environmental Molecular Science Institute, Boston, October 2-6, 2000.

R. M. Osgood,Jr., N. Camillone, K. Adib, D. Mocuta, "Photochemically promoted molecular rearrangement of organosulfur compounds adsorbed on semiconductor surfaces," Pacificchem 2000, Honolulu, Hawaii, December 14-19, 2000.

(d) Manuscripts submitted, but not published:

J.E. Spanier, M. Levy, I.P. Herman, R.M. Osgood, and A.S. Bhalla, "Single crystal, mesoscopic films of PZN-PT: formation and micro-Raman diagnosis," submitted to Applied Phys. Lett. (2001).

(e) JSEP Technical Reports submitted (1997-2000)

"Joint Services Electronics Program Annual Progress Report No. 48," for Grant DAAG5-97-1-0166 for the Period 1997-1998, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1998.

"Joint Services Electronics Program Annual Progress Report No. 49," for Grant DAAG5-97-1-0166 for the Period 1998-1999, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1999.

INVENTIONS

None

SCIENTIFIC PERSONNEL in Research Group of Professor Richard Osgood

Ahmad, R. U., GRA, PhD
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Kwak, H., Postdoc (Technical Solution)
Levy, M., Research Scientist (Professor, Michigan Technical University)
Mocuta, D., Postdoc (IBM)
Moryl, J., Research Scientist (Seton Hall)
Nagy, G., Postdoc (Intel)
Osgood, Jr., R. M., Professor, Principal Investigator
Radojevic, A. M., GRA PhD
Rao, H., GRA PhD
Scarmozzino, R., Research Scientist (Chief Technical Officer, RSoft)
Shen, X. J., GRA Ph.D (Computer Systems)
Smadici, S., GRA Ph.D.

1.2 ORDERED QUANTUM DOT THIN FILMS AND MATERIALS

Louis E. Brus, Principal Investigator
Research Area 1, Work Unit 2

(212) 854-4041

1.2A Self-Assembly of Nanocrystals

We explored the self-assembly properties of metallic and semiconductor nanocrystals, and the collective electrical and optical properties that result from self-assembly. We investigated 2D self-assembly on graphite surfaces, in order to explore fundamental questions of nanocrystal-solvent phase diagrams, and the interaction potential between two solvated nanocrystals. The observed bicontinuous patterns, as a function of surface coverage and drying time, imply that aggregation occurs by fluid-fluid spinodal nucleation and subsequent coarsening. Theoretically we investigated the nature of the van der Waals forces between mesoscopic objects. We also explored the mechanism of surface diffusion on graphite.

1.2B New Experimental Methods

We also developed new experimental methods for observation of single nanocrystals and nanotubes. We developed Electric Force Microscopy in order to detect the presence of a single charge on a single nanocrystal in a thin film at 23 C. Using an AFM modified to operate as a capacitor in non-contact mode, we detect the electric field gradient of one charge as a downshift in AFM cantilever resonant frequency. We have demonstrated that a single charge, either intrinsic or due to photoionization, can be observed with signal to noise of about five. This EFM method was also used to explore the electrostatic properties of self-assembled Trioctyl phosphine oxide layers on graphite.

1.2C Raman Scattering from Silver Nanocrystals

We have also carefully explored the Raman scattering of single Rhodamine 6G molecules on large Ag particles. While it has been known for 2 decades that there is an apparent local field Raman enhancement for molecules near Ag particles, we find that the Raman cross section is about 200 square Angstroms for Rhodamine molecules adsorbed in special sites. This is far larger than expected, and we believe it indicates the molecule is coupled to the transition dipole of the Ag particle by direct electron exchange. We are exploring a mechanism involving the interaction of ballistic electrons in the Ag with chemisorbed molecules at the junctions of two 50 nm particles. This work has been extended to nanocrystal dimers coupled by rigid linker molecules.

1.2D Raman Scattering from Single Carbon Nanotubes

Carbon nanotubes are probably the most novel physical system that has been discovered in the past decade. These tubes are the object of intense and accelerating study in the microelectronics community, as a possible physical system for "molecular electronics" many decades into the coming century. Synthetic methods make a broad mixture of tubes, of varying diameter and helicity. We carefully explored the Raman spectra of single nanotubes. We discovered that interference between the electronic and vibrational Raman scattering creates a Fano lineshape in the Resonance Raman Spectra. Via analysis of this scattering we should be able to understand the position of the Fermi level in metallic tubes, as a function of adsorbed surface molecules. We also were able to make structural assignments by analysis of the Stokes to anti-Stokes intensity ratio of the nanotube breathing mode, by use of a simple Resonance Raman model.

JSEP PUBLICATIONS AND PRESENTATIONS of Professor Louis Brus**3. Papers published in peer reviewed journals (1997-2001):**

- Louis Brus, "Semiconductor Nanocrystals as Molecules and Building Blocks", review article in *Modular Chemistry*, NATO ASI Ser.C, Vol 499 (J. Michl, ed., Kluwer Academic, Dordrecht, 1997), p. 303.
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- M. Nirmal and L. Brus, "Luminescence Photophysics in Semiconductor Nanocrystals", *Accounts of Chemical Research* 32, 407 (1999).
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(c) Papers presented at meetings, but not published in conference proceedings:

Major presentations "Physics and Chemistry of Mesoscopic Particles" with partial JSEP support:

Colloquium, Chemistry Dept., University of Maryland 2/4/98.

Colloquium, Physics Dept., City College of New York, 2/11/98.

Invited Talk, ACS National Meeting, Dallas, Texas, 3/30/98.

Colloquium, Physics Department, Columbia University, New York, NY, 4/24/98.

Physical and Materials Science Colloquium, Research Division, Bell Laboratories, NJ, 6/2/98.

Colloquium, Physics Department, University of Ohio, Toledo, Ohio, 9/2/98.

Colloquium, JILA, University of Colorado, Feb. 12, 1999.

Invited Talk, Optical Society of America Meeting, Santa Clara, Calif. Sept. 27, 1999.

Invited Talk, Gordon Conference on Nanocrystals, New London, Conn., July 28, 1999.

Chemistry Colloquium, Princeton University, May 28, 1999.

Introductory Talk, Gordon Conference on Nanoerystals, July 27, 1999.

Invited Talk, American Chemical Society National Meeting, New Orleans, August 23, 1999.

Optical Society of American National Meeting, Santa Clara, Calif. Sept. 28, 1999.

Atomic and Optical Physics Topical Meeting, JILA, Boulder, Colo., Oct. 28, 1999.

Chemistry Colloquium, Rutgers Univ. Newark, Oct. 15, 1999.

Harold Nation Lecture, Georgia Institute of Technology, Nov. 19, 1999.

Chemistry Division, Brookhaven National Laboratory, Feb. 16, 2000.

American Physical Society National Meeting, Minneapolis, March 22, 2000.

NSF sponsored Materials Research Science and Engineering Center Director's Meeting, University of Chicago, April 7, 2000.

NIH Conference on Nanotechnology, Washington DC, June 26, 2000.

International Conference on Solar Energy Conversion, Aspen, Aug. 1, 2000.

International Conference on Surface Enhanced Raman Scattering, Xiamen, China, Aug. 15, 2000.

Columbia Nanotechnology Symposium, Lerner Hall, Columbia University, Sept. 22, 2000.

Los Alamos Workshop on Complexity and Emergent Materials, Santa Fe, Jan. 8, 2001.

Chemistry Department, Long Island University, Feb. 13, 2001.

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(d) Manuscripts submitted, but not published:

Zhonghua Yu and Louis Brus, "(n,m) Structural Assignments and Chirality Dependence in Single-Wall Carbon Nanotube Raman Scattering", J. Phys. Chem. (accepted 2001).

(e) JSEP Technical Reports Submitted (1997-2000)

"Joint Services Electronics Program Annual Progress Report No. 48," for Grant DAAG5-97-1-0166 for the Period 1997-1998, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1998.

"Joint Services Electronics Program Annual Progress Report No. 49," for Grant DAAG5-97-1-0166 for the Period 1998-1999, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1999.

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2. ULTRAHIGH SPEED ELECTRONICS: NEW DEVICES AND PROBING TECHNIQUES

2.1 ULTRAFAST STUDIES OF ELECTRONIC MATERIALS AND DEVICES

Tony F. Heinz, Principal Investigator
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2.1A Generation of Ultrafast Electrical Pulses by Optical Rectification

The established approach for producing electrical transients using femtosecond optical excitation of photoconductors exhibits a fundamental limitation in response time, in the range of 0.5 ps, related to the transient dynamics of the photoexcited carriers. In addition, the photoconductive switch must be designed into the transmission line in advance and requires specialized processing steps or growth processes to achieve reduced carrier lifetimes that may be incompatible with other required fabrication steps. In investigations supported by the JSEP program, we have demonstrated a new approach to the production of ultrafast electrical signals on transmission lines that is flexible, non-invasive, and has the potential to produce electrical pulses whose duration is constrained only by that of the optical pulses. The new scheme that we have introduced involves the optical rectification process, an effect also mediated by the electro-optic response of the material. In this case, a short optical pulse passing through the nonlinear medium generates a polarization that follows the intensity envelope of the optical pulse. We have demonstrated that the transient polarization induced by an ultrafast optical pulse can be effectively coupled to a transmission line structure to produce an ultrafast electrical transient.

In our experiment, the generation process occurs in a LiTaO₃ nonlinear crystal bonded to a coplanar transmission line in a sliding contact geometry; phase coherent detection of the resulting electrical pulses on the transmission line is accomplished with a gated photoconductive switch integrated into the device. A bipolar temporal waveform with a width of 0.9 ps is measured after a propagation distance of a fraction of a mm. This pulselength is limited by the response time of the radiation damaged Si-on-sapphire-based photoconductive sampler. We observe both broadening and amplitude reduction in the temporal waveform due to propagation. A substantial improvement in both the bandwidth and amplitude is expected for a phase-matched geometry wherein both the optical and electrical pulses co-propagate along the transmission line. The present generation scheme may be used to inject electrical pulses at arbitrary points in a device or circuit. The combination of this approach with electro-optic sampling to reduce the detection response time will permit a compact all-optical spectroscopy system with extremely high bandwidths to be developed for transmission line measurements. The approach should also facilitate new measurements in circuit and device characterization.

2.1B Detection of the Vector Character of the Electromagnetic Field by Second-Harmonic Generation

A promising new optical technique for probing transient electric fields is that of optical second-harmonic generation (SHG). SHG has been employed to detect electrical pulses [1] and microwave signals in transmission line structure [2], as well as freely-propagating terahertz radiation [3]. The method, which utilizes the nonresonant material response of the sample, provides exceptional time resolution. The approach of field-induced SHG complements the powerful and well-established laser-based techniques of photoconductive sampling and the method of electro-optic sampling. The attractiveness of the SHG scheme lies in its simplicity and flexibility. For centrosymmetric materials, SHG permits direct optical probing of the field present in the sample without the introduction of external

crystals or special device structures. This property arises from the fact that the SHG process is forbidden (within the dipole approximation) in centrosymmetric materials, but becomes allowed in the presence of an electric field. Thus, in contrast to the linear optical response, the second-order nonlinear response of a centrosymmetric material is strongly influenced by the presence of relatively weak electric fields and measurements may be made in a simple reflection geometry.

Here we describe two recent advances that we have made in this method for probing electric fields: (i) A scheme for linearizing the relationship between the electric field and SHG intensity; and (ii) an approach for determining the vector nature of the electric field. Measurements have been carried out in silicon samples to illustrate these improvements in the technique experimentally. In our application of the method, we have also demonstrated the possibility of obtaining detailed spatially resolved 2-dimensional maps of the vector electric field distributions.

In order to understand the features of the EFISH technique, consider the behavior of the SH response observed for a static electric bias applied across the electrodes of Fig. 1. These data indicate the expected lack of a background signal in the absence of any bias field. Under application of a bias field, the relationship between the measured SH signal and the applied electric field E^0 is seen to be quadratic: $I_{2\omega} \propto (E^0)^2$. This expression reflects the linear relationship between the applied electric field E^0 and the nonlinear polarization, together with the quadratic relation between the SH intensity and the strength of the nonlinear polarization. Such a quadratic relation is clearly inconvenient, since it is more difficult to calibrate than a linear relationship. It also implies that information on the sign of E^0 is lost.

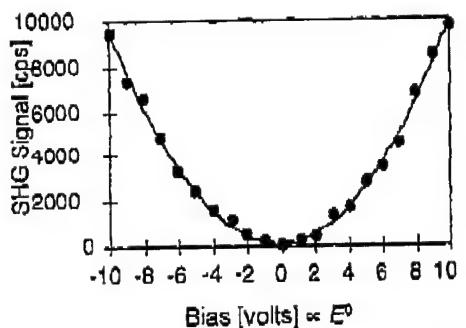


Fig. 1. Quadratic dependence of SH intensity with the applied bias voltage.

To characterize fully the applied electric field E^0 and linearize the relationship between the measured SH intensity and E^0 , we take advantage of interference techniques. In the present work we have applied a homodyne detection scheme [4]. In this approach, a reference SH field, E_{ref} is introduced that interferes with the SH field E_{sig} arising from the field-induced SH radiation. The total SH intensity then becomes

$$\begin{aligned} I_{2\omega} &\propto |E_{sig} + E_{ref}|^2 \\ &\approx E_{sig}^2 + E_{ref}^2 + 2E_{sig}E_{ref} \cos\varphi \end{aligned} \quad (1)$$

where φ is the relative phase between the two SH fields. In the limit of a strong reference field ($E_{ref} \gg E_{sig}$), the measured SHG is linear in E_{sig} , which is in turn proportional to E^0 , i.e.,

$$I_{2\omega} \propto E_{ref}^2 + 2E_{sig}E_{ref} \cos\varphi. \quad (2)$$

In our experiment, the reference field, E_{ref} , was provided by SHG from a z-cut quartz plate positioned before the sample.

Figure 2 shows the behavior of the total SH intensity over a large range of the bias voltage when the phase difference between E_{sig} and E_{ref} was arranged to yield $\varphi = 0$. The inset in the figure illustrates the case when $E_{ref} \gg E_{sig}$, which clearly demonstrates the expected highly linear dependence of the SHG signal on the bias voltage or applied electric field E_0 . In addition, we can establish the sensitivity of this technique to be $\sim 100 \text{ V/cm/Hz}^{1/2}$, which should be amenable to further optimization through improvements in laser and material parameters.

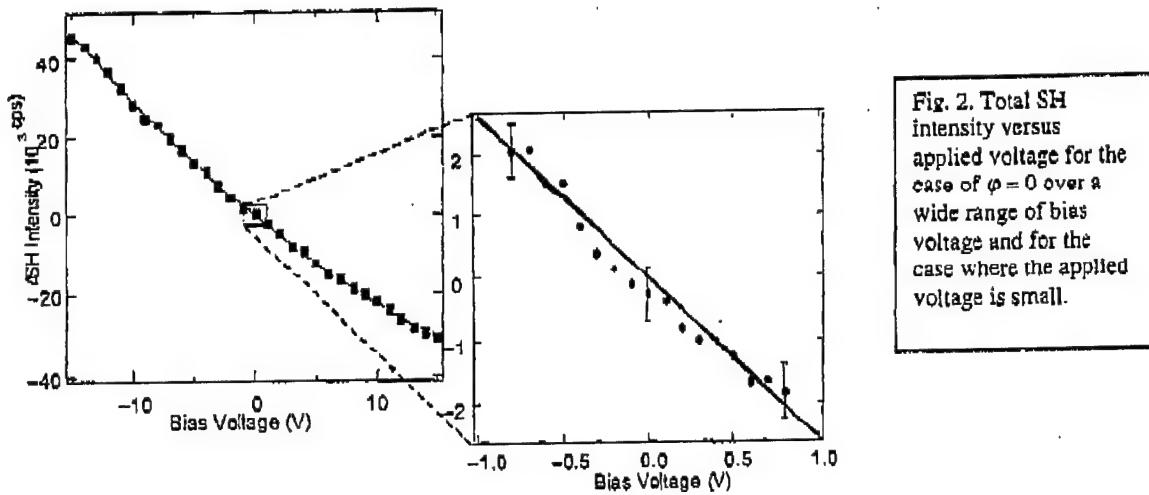


Fig. 2. Total SH intensity versus applied voltage for the case of $\varphi = 0$ over a wide range of bias voltage and for the case where the applied voltage is small.

We now wish to discuss the second improvement in the EFISH technique for probing electric fields and transients. This concerns measuring the vector character of the electric field. While previous studies have illustrated the sensitivity and time resolution of the method for probing the strength of the electric field, the potential for determination of the vector character of the electric field has not been examined. We have recently developed a scheme for such vector electric field measurements [5]. We illustrate the method by mapping the spatial distribution of the in-plane electric field in a silicon sample. By analyzing the tensor properties of the relevant nonlinear optical process in EFISH, we were able to develop a protocol for measuring the orthogonal components that compose the applied electric field. This could be accomplished simply by measuring the two orthogonal components of the field-induced SHG signal for normal incidence excitation. The approach was combined with the homodyne detection scheme described above to yield a linearized response.

Figure 3 shows experimental data for the electric field of a silicon-on-sapphire substrate patterned with aluminum lines. The electrode geometry consisted of $750 \times 750 \mu\text{m}^2$ rectangular pads that are separated by $80 \mu\text{m}$. For purposes of illustration, a bias voltage of 360 V, corresponding to an average electric field strength of approximately 45 kV/cm , was applied across the electrodes. The electric field components were sampled by scanning along the x -axis for each y -position at $10 \mu\text{m}$ increments in a square grid. The optical SHG measurements were made with a modelocked Ti:sapphire laser.

In the resulting vector field map note that in the area between the electrodes, the electric field is relatively uniform and aligned along the x -direction. We attribute the weak irregularities in the electric

field direction seen in certain spatial regions to local imperfections and inhomogeneities in the substrate and electrode structure. In the region beyond the end of the electrodes, we observe the expected fringing pattern. The electric field in this region has both x and y components, which can be comparable, especially near the corners of the electrodes. Because of the finite spatial resolution of the SHG probe, the inferred amplitude of the electric field at grid points adjacent to the electrodes is reduced and, conversely, finite values for the electric field are found for grid points just inside the electrodes. Well inside the electrodes, no electric field was detected within experimental uncertainty.

It is anticipated that this approach will find application in analysis of high-speed electronic and optoelectronic devices.

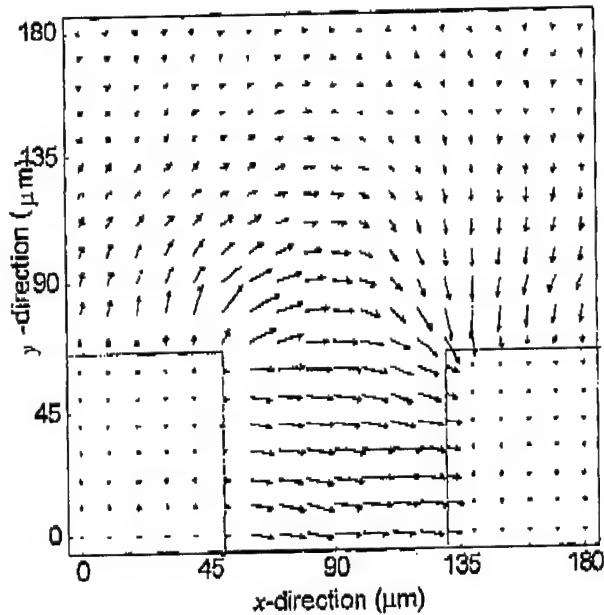


Fig. 3. Experimental results from field-induced SHG measurement: vector map of the electric field distribution at the end of a pair of metal electrodes deposited on a silicon-on-sapphire substrate.

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(b) Papers published in non-peer-reviewed journals or in conference proceedings:

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(c) Papers presented at meetings, but not published in conference proceedings:

- T. F. Heinz, "Probing Transient Electric Fields with Nonlinear Optics," Conference on Macroscopic and Microscopic Characterizations of Semiconductor Surfaces and Interfaces, Austin, TX, 4/20 - 4/21/98 (Invited).
- A. Nahata and T. F. Heinz, "Generation of Subpicosecond Electrical Pulses Using Optical Rectification," Conference on Lasers and Electro-Optics (CLEO'97), Baltimore, MD, 5/18 - 5/23/97.
- T. F. Heinz, "Generation and Detection of Ultrafast Electric Fields Using Nonlinear Optics," International Conference on Coherent and Nonlinear Optics - ICONO XVI, Moscow, Russia, 6/29 - 7/3/98 (Invited).
- A. Nahata and T. F. Heinz, "Detection of Terahertz Pulses Using Optical Second-Harmonic Generation," IEEE Lasers and Electro-Optics Society 1997 Annual Meeting (LEOS'97), San Francisco, CA, 10/11 - 13/11/97.
- T. F. Heinz, "Ultrafast Optoelectronics Using Nonlinear Optics," Optical Society of America Annual Meeting, Long Branch, CA, 10/13 - 10/17/97 (Invited).
- A. Nahata and T. F. Heinz, "Ultrafast Optoelectronics Using Nonlinear Optics," IEEE Lasers and Electro-Optics Society Annual Meeting - LEOS '98, Orlando, FL, 12/1 - 12/4/98 (Invited).
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(d) Manuscripts submitted, but not published:

None

(e) JSEP Technical Reports Submitted (1997-2000):

"Joint Services Electronics Program Annual Progress Report No. 48," for Grant DAAG5-97-1-0166 for the Period 1997-1998, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1998.

"Joint Services Electronics Program Annual Progress Report No. 49," for Grant DAAG5-97-1-0166 for the Period 1998-1999, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1999.

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3. MATERIALS PROCESSING AND DIAGNOSTICS FOR ADVANCED ELECTRONIC MATERIALS

3.1 ELECTRONIC AND STRUCTURAL PROPERTIES OF SURFACES AND SURFACE ADSORBATES USING SCANNING TUNNELING MICROSCOPY (Controlling Chirality of Interfacial Films)

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Research Area III, Work Unit 1

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3.1A Packing of $\text{Br}(\text{CH}_2)_{10}\text{COOH}$ and $\text{Br}(\text{CH}_2)_{11}\text{COOH}$ on Graphite: An Odd-Even Length Effect Observed by Scanning Tunneling Microscopy

Scanning Tunneling Microscopy (STM) is a powerful tool for studying molecular ordering at the liquid-solid interface.¹ Early STM studies of singly substituted long chain alkane molecules at the solution-substrate interface have shown that different functional groups can have important effects on molecular ordering. For example, n-alkanes²⁻⁴ form lamellar structures on graphite with their molecular axis perpendicular to the lamellar boundary; 1-alcohols have a 60° angle between their molecular axes and the lamellar direction;⁵⁻⁸ 1-carboxylic acid molecules^{6,7} assume an interdigitating structure; and 1-bromo- and chloro- alkanes⁸ take the same surface arrangement as the n-alkanes. Thus, the end groups of these molecules play a pivotal role in their packing pattern.

STM has been used to investigate doubly substituted 11-bromoundecanoic acid, $\text{Br}(\text{CH}_2)_{10}\text{COOH}$, and 12-bromododecanoic acid, $\text{Br}(\text{CH}_2)_{11}\text{COOH}$, where it was observed that chain length, in particular even and odd numbers of carbon atoms, can have a significant impact on thin film, interfacial ordering.⁹ The absolute conformations of these molecules have been determined unambiguously. Both molecules adopt structures different from their monosubstituted counterparts. The packing structure of these molecules on the surface has been found to be significantly affected by whether the hydrocarbon chain has an odd or even number of carbon atoms. A simple geometric effect and molecular model have been used to explain the source of this difference.

3.1B Direct Determination of The Chirality of Organic Molecules Adsorbed At Liquid-Solid Interfaces Determined By Scanning Tunneling Microscopy

In some cases^{6,7} STM has achieved atomic resolution allowing the relative position of individual atoms in a molecule to be clearly observed. Given this sensitivity, SPM seems to be a promising method for determining the absolute configuration of chiral molecules. Indeed some progress has been made in this direction. By using atomic force microscopy (AFM), a few chiral enantiomers of chiral biphenylbenzoates have been found by STM to give different 2-D chiral images; however, the molecular resolution obtained in these studies did not allow the direct assignment of the absolute configuration of the individual enantiomers.^{12,13} Recently, there has been a beautiful demonstration of the principles of chiral HPLC using chemical force microscopy.¹⁴

In our study atomically resolved STM images of 2-bromohexadecanoic acid adsorbed on a graphite surface provide a direct assignment of single molecules as having R or S chiral centers through the use of STM "marker" chemical groups and atoms.¹⁵ The chiral molecules, (R)/(S)-2-

bromohexadecanoic acid, adsorbed on the graphite surface have been imaged by STM with atomic resolution. These two enantiomers segregate on the graphite surface and form different, pure R or S domains. The two enantiomers give mirror image packing patterns on the graphite surface. The absolute configuration of these molecules can be directly observed in the STM images.

3.1C Controlling Chirality of Interfacial Films

The chirality of individual molecules has been determined and investigated using scanning probe methodologies in the studies of 2-bromohexadecanoic acid¹⁵ and the asymmetric induction of alkenes on a silicon surface.^{16,17} It is now appropriate to ask how the self-assembly of chiral molecules is affected by the presence of other non-chiral species. De Feyter et. al.¹⁸ have studied monolayers of enantiomerically pure isophthalic acid derivatives coadsorbed with the achiral solvent 1-heptanol onto a graphite surface. The effect of a third element (a coadsorbate in the form of another solute), however, has not been previously studied. Such achiral coadsorbates show promise as powerful tools to segregate chiral molecules and control self-assembled monolayers.

The self-assembly of a mixture of achiral hexadecanoic acid with racemic 2-Br-hexadecanoic acid has been investigated in our laboratory using scanning tunneling microscopy.¹⁹ Hexadecanoic acid has the ability to control the two-dimensional structure formed at the interface by creating a template that sets the angle between the molecular and lamellar axes in the mixed monolayer. Further, inherently achiral hexadecanoic acid self-assembles on the graphite surface into two distinct, although almost indistinguishable domains that exhibit mirror image morphology, similar to that observed for other even-numbered fatty acids.¹¹ This property leads to resolution of (R)/(S)- 2-Br-hexadecanoic acid into enantiomerically pure (R and S) domains when physisorbed onto a graphite surface from the mixture. Achiral molecules such as hexadecanoic acid are, thus, shown to have remarkable potential as tools to manipulate self-assembly and more specifically, to induce enantiomeric resolution of racemic mixtures like 2-bromohexadecanoic acid.

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(b) Papers published in non-peer-reviewed journals or in conference proceedings:

None

(c) Papers presented at meetings, but not published in conference proceedings:

G. W. Flynn, "Quenching Molecules with Chemically Significant Vibrational Energy: Super Collisions and Probability Distributions," Department of Energy, Combustion Contractors Meeting, Chantilly, VA, May 31, 1997.

G. W. Flynn, "Experimental Determination of the Collisional Energy Transfer Probability Distribution," Cornell University, Ithaca, NY, October 8, 1997; U. of California, Berkeley, CA, November 11, 1997.

G. W. Flynn, "STM Investigation of the Structure and Dynamics of Long Chain Molecules Adsorbed at the Liquid-Solid Interface," Pacific Northwest Nat'l Labs, Richland, WA, January 6, 1998. G. W. Flynn and H. Charles Tapalian, "Using Infrared Lasers to Probe Molecular Interactions," Electro-optics Seminar, Charles Stark Draper Laboratory, Cambridge, MA, February 17, 1998.

G. W. Flynn, "STM Investigation of the Structure and Dynamics of Long Chain Molecules Adsorbed at the Liquid-Solid Interface," Wayne State University, Detroit, MI, February 23, 1998.

G. W. Flynn and Eric T. Sevy, "Energy-transfer distribution functions of highly vibrationally excited methylpyrazine from state-resolved collisional energy-transfer data," E. T. Sevy and G. W. Flynn, 215th National ACS Meeting, Dallas, TX, April 1, 1998.

G. W. Flynn, "Collisional Energy Transfer in Molecules with Chemically Significant Vibrational Energy," Symposium on Combustion Dynamics, American Chemical Society National Meeting, Dallas, TX, April 1, 1998.

G. W. Flynn and H. Charles Tapalian, "Infrared Pumping of Molecular Vibrations," Physical Chemistry Seminar, Columbia University Department of Chemistry, April 20, 1998.

G. W. Flynn and Seth Rubin, "Round 'em Up': The Use of Molecular Corrals in Scanning Tunneling Microscopy Studies of Docosane Bromide Conformations," S. M. Rubin, L. C. Giancarlo, H. Fang, D. M. Cyr and G. W. Flynn, NY Section of the American Chemical Society Meeting, NY, NY, May 2, 1998.

G. W. Flynn, "STM Investigation of the Structure and Dynamics of Long Chain Molecules Adsorbed at the Liquid-Solid Interface," University of Pittsburgh, Pittsburgh, PA, May 7, 1998.

G. W. Flynn and Hongbin Fang, "STM studies of the structure, dynamics and reactions of long chain hydrocarbon molecules at the liquid-solid interface," Gordon Research Conference on Electronic Process of Organic Materials, July 26-July 31, 1998.

G. W. Flynn and Leanna C. Giancarlo, "Scanning Tunneling Microscopy Investigation of the Influence of the Substrate on Monolayer Order and Molecular Image Contrast," Fuctionalized Hydrocarbons Physisorbed on Graphite and MoS₂," L. C. Giancarlo, H. Fang, S. M. Rubin, A. A. Bront and G. W. Flynn, 216th American Chemical Society Meeting, Physical Division, Boston MA, August, 1998.

G. W. Flynn, "Scanning Tunneling Microscopy of Molecules Adsorbed at the Liquid-Solid Interface," Symposium on the Structure and Electronic Properties of Materials by Scanning Probe Microscopy, American Chemical Society National Meeting, Boston, MA, August 24, 1998.

G. W. Flynn, "Scanning Tunneling Microscopy at Liquid-Solid Interfaces," (invited) University of Chicago, Chicago, IL, April 26, 1999.

- G. W. Flynn, " Scanning Tunneling Microscopy at Liquid-Solid Interfaces," (invited) Rowland Institute for Science, Cambridge, MA, May 6, 1999.
- G. W. Flynn, "Quenching Molecules with Chemically Significant Amounts of Energy," XVI Conference on Molecular Energy Transfer, Assisi, Italy, June 20-25, 1999.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," (invited) MIT, Cambridge, MA, November 2, 1999.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," (invited) University of Maryland, College Park, MD, November 4, 1999.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," Department of Physics, Columbia University, New York, NY, February 25, 2000.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," Symposium on New Techniques in Surface/Interface Science Experimental Studies of Chirality at Interfaces Using Scanning Probe Microscopy American Physical Society National Meeting, Minneapolis, MN, March 21, 2000.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," American Chemical Society National Meeting, San Francisco, CA, March 28, 2000, Symposium on Physical Aspects of Chirality.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," (invited) University of Oklahoma, Norman, OK, April 6, 2000.
- G. W. Flynn, " Quenching Molecules with Chemically Significant Vibrational Energy: Super Collisions and Probability Distributions," (invited) University of Oklahoma, Norman, OK, April 7, 2000.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," Harvard Club of New York, May 24, 2000.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," City University of New York, New York, NY, September 20, 2000.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," State University of New York at Stony Brook, Stony Brook, NY, February 22, 2001.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," Syracuse University, Syracuse, NY, April 24, 2001.
- G. W. Flynn, "Raising Flags: Chemical Marker Group STM Probes of Self Assembly and Chirality at Liquid-Solid Interfaces," Scanning 2001, Symposium on Nanotechnology and Nanofabrication, New York, NY, May 5, 2001.

(d) Manuscripts submitted, but not published:

None

(e) JSEP Technical Reports submitted (1997-2000):

"Joint Services Electronics Program Annual Progress Report No. 48," for Grant DAAG5-97-1-0166 for the Period 1997-1998, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1998.

"Joint Services Electronics Program Annual Progress Report No. 49," for Grant DAAG5-97-1-0166 for the Period 1998-1999, submitted to the Joint Services Technical Coordinating Committee by Columbia University, Columbia Radiation Laboratory, December 1999.

INVENTIONS

None

SCIENTIFIC PERSONNEL in Research Group of Professor George Flynn

Graduate Research Assistants:

Hongbin Fang (Ph.D., 1998)
Chris A. Michaels (Ph.D., 1997)
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Dalia Yablon (GRA, Ph.D.)

Post-doctoral Fellows:

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H. Charles Tapalian

Undergraduates:

Seth Rubin
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3.2 NEW OPTICAL MATERIALS, SOURCES, AND METHODS

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Research Area 3, Work Unit 2

3.2A Processing, Physics and Applications of Porous SiC

The preparation and properties of porous SiC were studied in a series of experiments. The optical transmission, temperature-dependence of the photoluminescence (PL), and Raman scattering of porous SiC prepared from *p*-type 6H-SiC were compared with those from bulk *p*-type 6H-SiC. While the transmission spectrum of bulk SiC at room temperature revealed a relatively sharp edge corresponding to its band gap at 3.03 eV, the transmission edge of porous SiC (PSC) is too wide to determine its band gap. It is believed that this wide edge might be due to surface states in PSC. At room temperature, the PL from PSC is 20 times stronger than that from bulk SiC. The PL PSC spectrum is essentially independent of temperature. The relative intensities of the Raman scattering peaks from PSC are largely independent of the polarization configuration, in contrast to those from bulk SiC, which suggests that the local order is fairly random.[1]

The reflectance of PSC thin films on SiC substrates was measured in the infrared reststrahlen region by Fourier transform infrared reflectance spectroscopy and compared to simulated spectra based on phenomenological and Bergman statistical effective-medium dielectric functions. The phenomenological models evaluated include the Bruggeman, cavity- and sphere-Maxwell-Garnett (C-MG and S-MG), Landau-Lifshitz/Looyenga (LLL), and Monecke models. In addition, modifications to the Bruggeman and C-MG models with variable particle shapes and surface layers were examined. Hybrid versions of the C-MG and LLL models were also considered, alternatively by using a phenomenological mixing approach, which gives a direct physical interpretation of the topology, and by directly mixing the statistical spectral density functions of the C-MG and LLL effective dielectric functions. This latter statistical hybrid model gave the best (and quite good) agreement with experiments (Fig. 1). The differences in the hybrid models can be understood by comparing their spectral density functions. The dip (or splitting) in the PSC film reststrahlen band is attributed to a wide spectrum of surface optical phonon modes.[2]

The infrared reflectance from PSC prepared in *n*-type SiC, both as-anodized and passivated, was also studied. The passivation of PSC was accomplished using a short thermal oxidation. Fourier transform infrared (FTIR) reflectance spectroscopy was employed *ex situ* after different stages of the thermal oxidation process. The characteristics of the reststrahlen band normally observed in bulk SiC are altered by anodization; further changes in the reflectance spectra occurred following oxidation for different periods of time. An effective medium theory model that includes air, SiC and SiO₂ as component materials was shown to characterize the observed changes in the reflectance spectra after different stages of PSC oxidation.[3]

SiC vapor-phase epitaxy on PSC substrates formed by electrochemical anodization was demonstrated. Polarized micro-Raman scattering indicated that the polytype of the optically smooth SiC grown on PSC formed in both *p*-type and *n*-type 6H-SiC substrates is 6H. The Raman scattering selection rules in these films are the same as those observed in the bulk substrate and epilayers grown on bulk, indicating high crystalline quality (Fig. 2). The formation of epitaxial 6H-SiC on porous 6H-SiC may open up new possibilities for dielectric device isolation, fabrication, and epitaxial lift-off.[4]

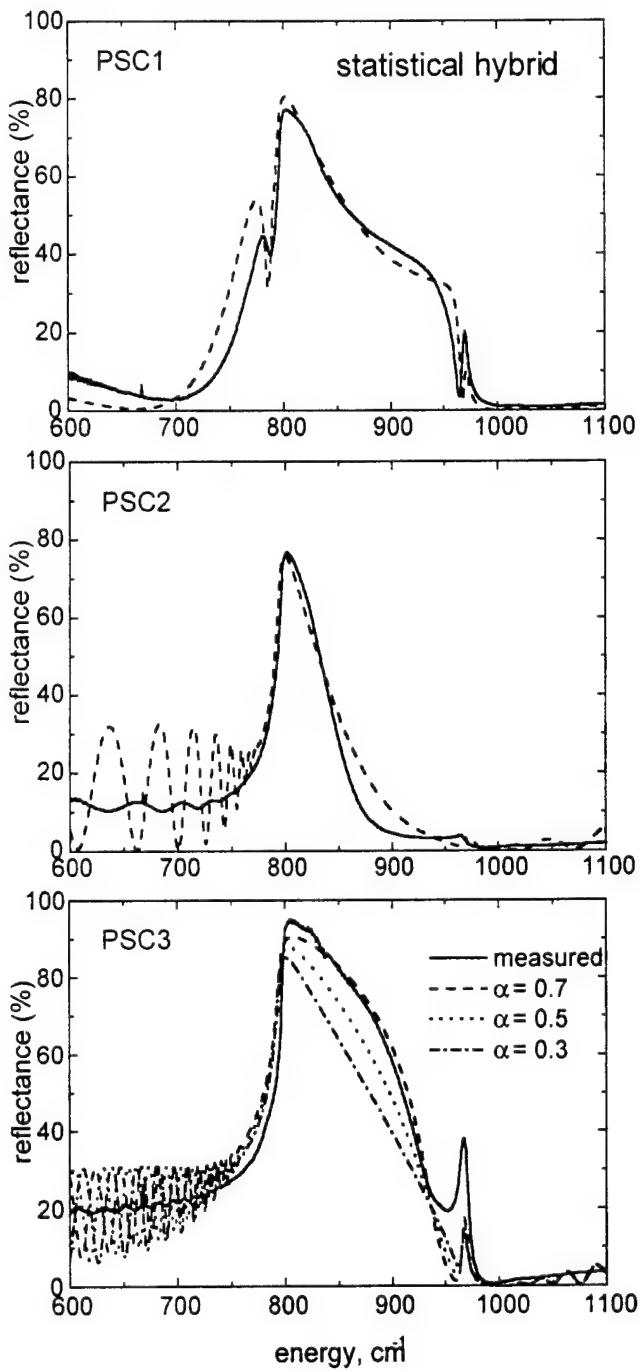


Fig. 1. Modeled reflectance from PSC films on SiC substrates using the Bergman statistical hybrid model with $\alpha = 0.5$ (dashed lines) for the three PSC films; the measured reflectance is denoted by the solid lines. For comparison, model fits for $\alpha = 0.3$ and 0.7 are also shown for PSC3.

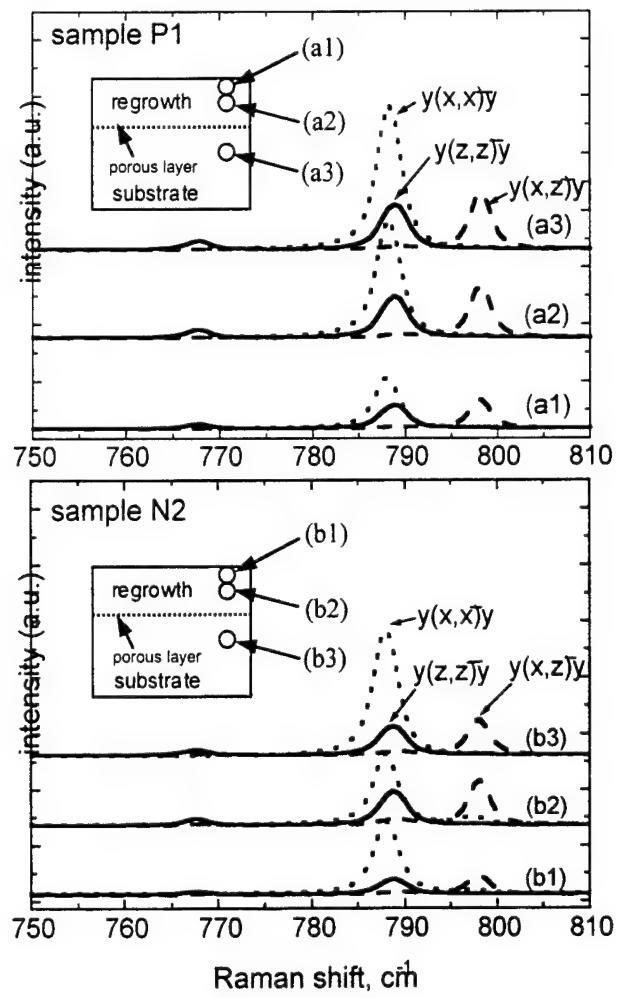


Fig. 2. Cross-section polarized Raman spectra of SiC on porous (a) sample P1, and (b) sample N2. The solid, dashed, and dotted lines denote the $y(z,z)\bar{y}$, $y(x,z)\bar{y}$ and $y(x,x)\bar{y}$ configurations, respectively. The spectra have been taken near the top surface in (a1) and (b1), near the center of the regrown layer in (a2) and (b2), and within the underlying bulk substrate in (a3) and (b3).

3.2B Properties and Processing of Oxide and Large Band-Gap Semiconductor Films

In a collaboration with Prof. Osgood's group, a novel process to form thin films of lead zinc niobate - lead titanate (PZN-PT) from a bulk crystal for microelectronic and microelectromechanical device applications was studied. The structural phase transitions and ferroelectric ordering in unpoled crystalline bulk and thin film relaxor PZN-PT were studied from -190°C to 600°C using polarized micro-Raman scattering. The structural phase transitions in this material were observed by distinct changes in the polarization selectivity (Fig. 3). The results for the thin film and the bulk crystal were found to be in good agreement for a wide range of the temperatures studied, indicating that the thin-film PZN-PT retains much, if not all, of the structural and ferroelectric properties of the original bulk substrate.[5]

In a collaboration with Prof. Neumark's group, the optical and structural properties of the δ -doped ZnSe:Te system were studied using photoluminescence (PL), x-ray and polarized Raman scattering. The Herman group did the Raman studies in this work. All of these samples are of reasonable crystalline quality and have the symmetry of the host ZnSe lattice as determined by x-ray diffraction and Raman scattering.[6] As part of this collaboration, evidence of isoelectronic traps were found in MBE grown $Zn_{1-x}Be_xSe$, using photoluminescence (PL). Studies of the PL as a function of pressure in a diamond anvil cell confirmed that this state is linked to the band transition.[7] In several samples of GaN films, highly unusual and reversible decay and enhancement of PL was also studied.[8]

3.2C Properties of Arrays of CdSe Nanoparticles

Three-dimensional arrays of organically passivated CdSe nanocrystals were investigated under hydrostatic pressure using photoluminescence (PL) and absorption spectroscopies. Interdot separations were varied coarsely by varying the organic ligand on the nanocrystal and finely by applying hydrostatic pressure. The PL and absorption spectra of solutions and arrays of CdSe nanocrystals capped by either tri-n-octylphosphine oxide (TOPO) or tri-n-butylphosphine oxide (TBPO) are the same up to 60 kbar, which suggests that they exhibit no interdot coupling since the interdot separation in the solutions (~50 nm) are much greater than those in the arrays (<1 nm). While the variation with pressure is roughly that expected from the increase in band gap energy of bulk CdSe with pressure and the increase in confinement energies of electrons and holes with increased pressure, there is still a significant difference in the energy of the PL peak and the first exciton in absorption (the Stokes shift) for both these solutions and arrays that increases with pressure (Figs. 4 and 5). This is attributed mostly to increased vibrational relaxation due to the movement of nuclei in the excited state. In contrast, there is a distinct difference between the pressure dependence of CdSe/pyridine dots in solution and arrays; the increase of the energy of the first exciton peak in absorption with pressure becomes markedly slower above about 30 kbar in CdSe/pyridine arrays, and is lower than that in the corresponding solution by ~ 50 meV at 50 kbar and ~70 meV at 60 kbar (Fig. 6). Experiments with CdSe/shell/pyridine dots, with large electron and hole barriers, cast doubt on the mechanism of interdot electron and/or hole tunneling leading to a decrease in electron and/or hole confinement energy. Also, interdot tunneling of single carriers may be inhibited by the charge separation energy. The differences in the dielectric medium surrounding each dot in the solution and array explain their different absorption exciton energies at ambient pressure, but not the changes at elevated pressure.[9]

The observed loss of much of the pyridine ligands during array drying could be very significant, and contact between pyridine-capped dots at elevated pressure may be important. Using FTIR ATR, it was shown that only about 30% of the pyridine ligands remain after three days of drying (Figs. 7 and 8).[10]

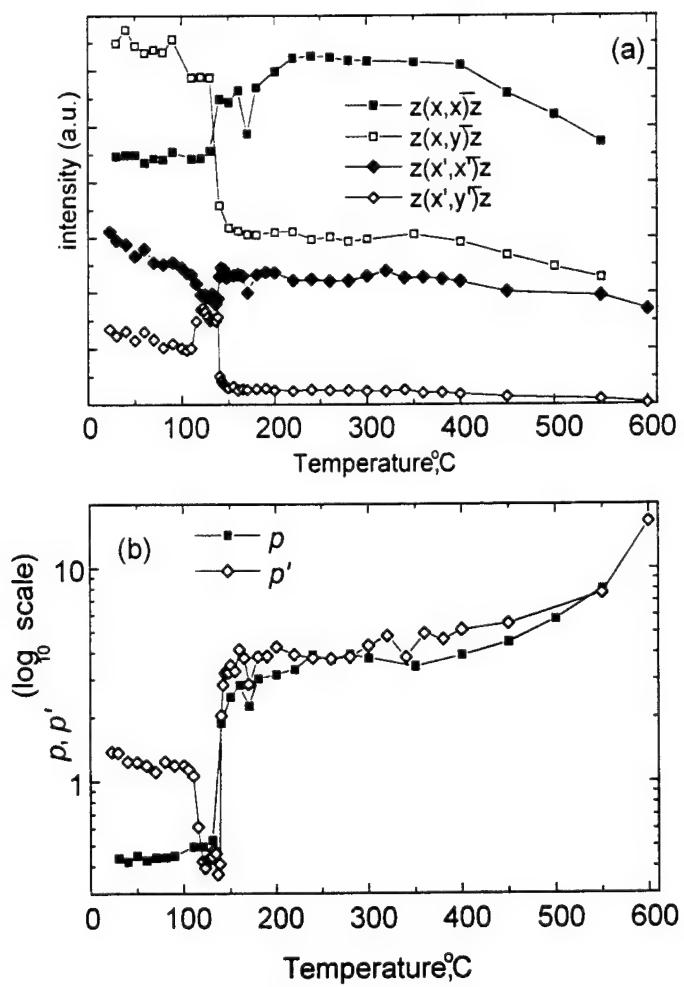


Fig. 3. (a) Raman scattering intensities of the $\sim 780 \text{ cm}^{-1}$ line for the bulk sample for the $z(x, \bar{x})\bar{z}$, $z(x, \bar{y})\bar{z}$, $z(x', \bar{x}^T)\bar{z}$, and $z(x', \bar{y}^T)\bar{z}$ configurations, and (b) the polarization ratios p (solid squares) and p' (open diamonds) plotted as functions of temperature. The intensities are offset for clarity, and the polarization ratios are on a log scale.

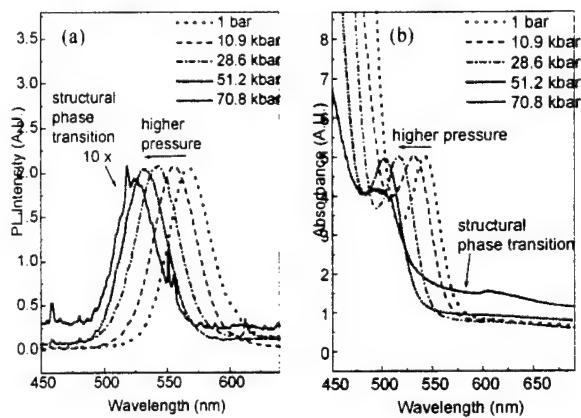


Fig. 4. (a) PL and (b) absorption spectra of CdSe/CdS/TBPO nanocrystal arrays as a function of pressure; for clarity only selected spectra at intermediate pressures are shown. These spectra are fairly typical for CdSe nanoparticles capped by TOPO or TBPO in dilute solution or in an array. Note the structural phase transition from wurtzite to rock salt above 65 kbar.

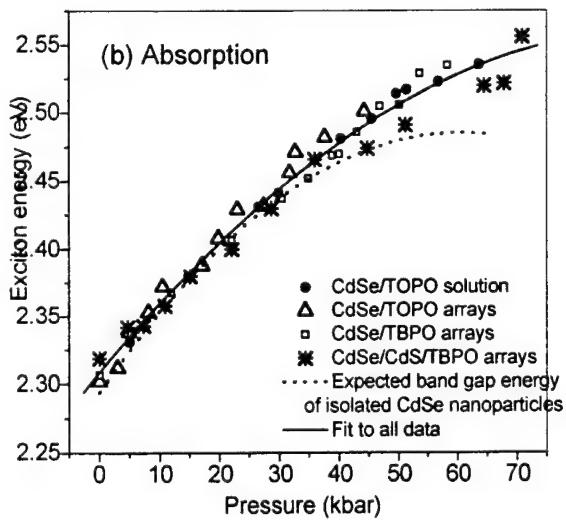
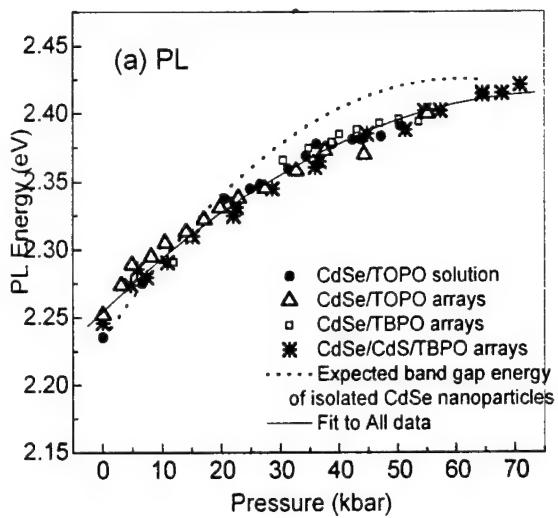


Fig. 5. (a) Peak energy of PL and (b) the first excitonic peak energy of the absorption spectra vs. pressure for solutions and arrays of CdSe nanocrystals capped by either TOPO or TBPO. Each plot in each figure has been shifted vertically by up to ~ 10 meV so that each overlaps at 1 bar. The solid curve is a least-squares fit to the data in each part. The expected band gap energy of isolated CdSe nanocrystals vs. P is plotted in both parts, which accounts for changes in the bulk band gap and confinement energies.

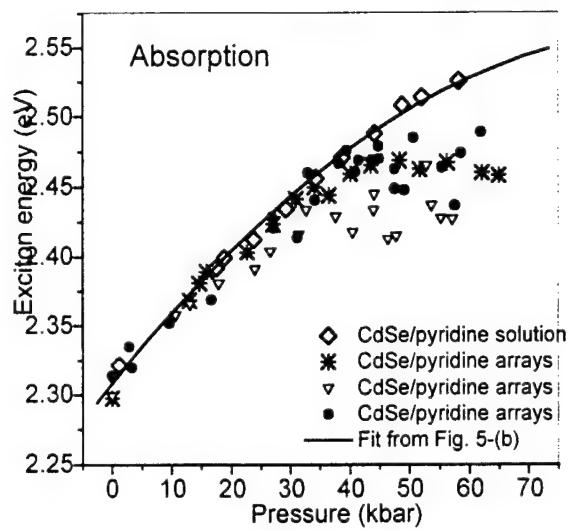


Fig. 6. The first excitonic peak energies in absorption spectra for several CdSe/pyridine runs. Note the significant difference between the solution and the array runs. Each plot has been shifted by up to ~ 10 meV so that each overlaps at 1 bar. The solid line is the fit to the exciton absorption data in (and also plotted in) Fig. 5-(b).

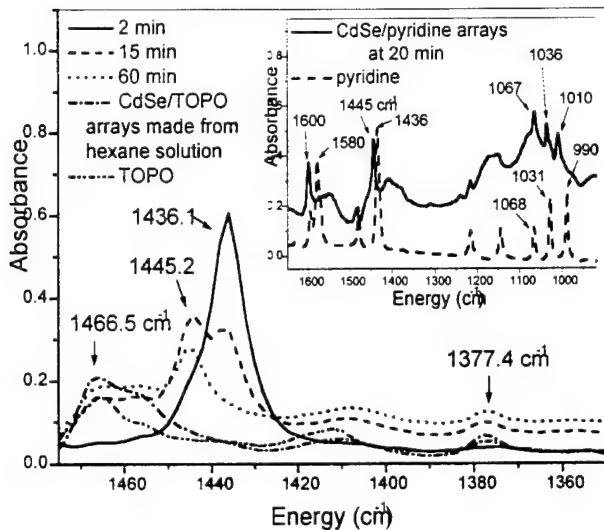


Fig. 7. ATR spectra of CdSe/pyridine arrays formed with pyridine solvent 2, 15, and 60 min. into self-assembly, along with those of pure TOPO and a CdSe/TOPO array formed with hexane solution. The inset shows spectra of CdSe/pyridine arrays after 20 min. and neat pyridine.

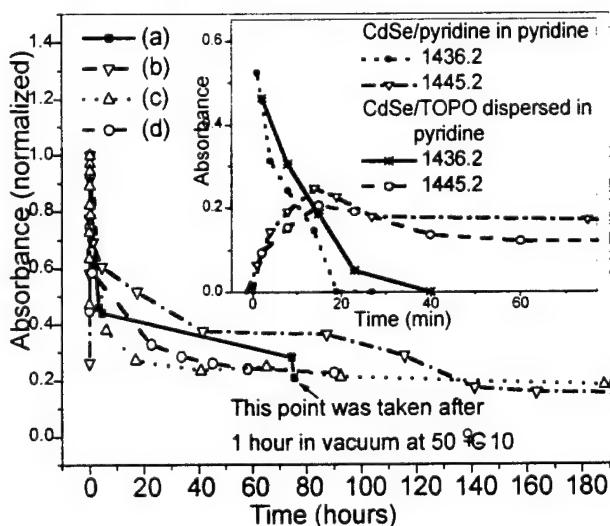


Fig. 8. Heights of 1445 cm⁻¹ peaks in the ATR spectra of (a), (b), and (c) CdSe/pyridine arrays from pyridine solution and (d) CdSe/TOPO arrays from pyridine solution as a function of drying time, normalized to unity at the maximum of each trace. The inset shows this (unnormalized) on a finer time scale at 1445 cm⁻¹ (bound pyridine) and also at 1436 cm⁻¹ (neat pyridine).

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1. Sangsig Kim, Jonathan E. Spanier, and Irving P. Herman, "Optical transmission, photoluminescence, and Raman scattering of porous SiC prepared from p-type 6H-SiC", Jpn. J. Appl. Phys. 39, 5875 (2000).
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3. Jonathan E. Spanier and Irving P. Herman, "Infrared reflection spectroscopy and effective medium modeling of as-anodized and oxidized porous silicon carbide", J. Porous Mater. 7, 139 (2000).
4. Jonathan E. Spanier, Greg T. Dunne, Larry B. Rowland, and Irving P. Herman, "Vapor-phase epitaxial growth on porous 6H-SiC analyzed by Raman scattering", Appl. Phys. Lett. 76, 3879 (2000).
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6. Igor L. Kuskovsky, C. Tian, G. F. Neumark, J. E. Spanier, Irving P. Herman, W.-C. Lin, S. P. Guo, and M. C. Tamargo, "Optical properties of δ -doped ZnSe:Te grown by molecular beam epitaxy: the role of tellurium", Phys. Rev B 63, 155205 (2001).
7. B. S. Kim, I. L. Kuskovsky, C. Tian, I. P. Herman, and G. F. Neumark, "Evidence of Isoelectronic Traps in Molecular Beam Epitaxy Grown $Zn_{1-x}Be_xSe$: Temperature- and Pressure-Dependent Photoluminescence Studies", accepted to Appl. Phys. Lett. (2001).
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9. B. Kim, M. Islam, L. Brus, and I. P. Herman, "Interdot Interactions and Band Gap Changes in CdSe Nanocrystal Arrays at Elevated Pressure," accepted, in press, J. Appl. Phys. 89, xxx (June 15, 2001).
10. B. Kim, L. Avila, L. Brus, and I. P. Herman, "Organic Ligand and Solvent Kinetics during the Self Assembly of CdSe Nanocrystal Arrays using Infrared Attenuated Total Reflection," Appl. Phys. Lett. 76, 3715-3717 (2000).

JSEP PUBLICATIONS AND PRESENTATIONS of Professor Irving Herman

(a) Papers published in peer reviewed journals (1997-2001):

- R. Eryigit and I. P. Herman, "Optical Anisotropy of the GaAs(001) Surface," Phys. Rev. B 56, 9263 (1997).
- H. Fang, J. Eng, Jr., C. Su, S. Vemuri, I. P. Herman, and B. E. Bent, "Real-Time Monitoring of the Etching of GaAs(100) by Surface Photoabsorption," Langmuir 14, 1375 (1998).
- J. E. Spanier and I. P. Herman, "Infrared Reflection Spectroscopy of as-Anodized and Passivated 6H and 4H Porous Silicon Carbide," Mater. Res. Soc. Symp. Proc. 486, 317 (1998).
- B. Kim, I. Kuskovsky, I. P. Herman, D. Li, G. Neumark, and J. Redwing, "Reversible Ultraviolet-induced Photoluminescence Degradation and Enhancement in GaN Films," J. Appl. Phys. 86, 2034 (1999).
- Sangsig Kim, Jonathan E. Spanier, and Irving P. Herman, "Optical transmission, photoluminescence, and Raman scattering of porous SiC prepared from p-type 6H-SiC", Jpn. J. Appl. Phys. 39, 5875 (2000).
- Jonathan E. Spanier and Irving P. Herman, "Use of hybrid phenomenological and statistical effective-medium theories of dielectric functions to model the infrared reflectance of porous SiC films", Phys. Rev. B 61, 10437 (2000).
- Jonathan E. Spanier and Irving P. Herman, "Infrared reflection spectroscopy and effective medium modeling of as-anodized and oxidized porous silicon carbide", J. Porous Mater. 7, 139 (2000).
- Jonathan E. Spanier, Greg T. Dunne, Larry B. Rowland, and Irving P. Herman, "Vapor-phase epitaxial growth on porous 6H-SiC analyzed by Raman scattering", Appl. Phys. Lett. 76, 3879 (2000).
- Jonathan E. Spanier and Irving P. Herman, "Use of hybrid phenomenological and statistical effective-medium theories of dielectric functions to model the infrared reflectance of porous SiC films", Phys. Rev. B 61, 10437 (2000).
- B. Kim, L. Avila, L. Brus, and I. P. Herman, "Organic Ligand and Solvent Kinetics during the Self Assembly of CdSe Nanocrystal Arrays using Infrared Attenuated Total Reflection," Appl. Phys. Lett. 76, 3715-3717 (2000).
- Igor L. Kuskovsky, C. Tian, G. F. Neumark, J. E. Spanier, Irving P. Herman, W.-C. Lin, S. P. Guo, and M. C. Tamargo, "Optical properties of δ -doped ZnSe:Te grown by molecular beam epitaxy: the role of tellurium", Phys. Rev B 63, 155205 (2001).

(b) Papers published in non-peer-reviewed journals or in conference proceedings:

None

(c) Papers presented at meetings, but not published in conference proceedings:

Papers presented at meetings identifying JSEP support:

- I. P. Herman, "Optical Properties of as-Anodized and Passivated 6H and 4H Porous Silicon Carbide," Materials Research Society Fall Meeting, Presentation H12.2, Boston, December 3, 1997, with J. E. Spanier.
- B. Kim, I. P. Herman, D. Li, I. Kuskovsky, G. F. Newmark, and J. M. Redwing, "Ultraviolet-induced Photoluminescence Degradation and Enhancement in GaN," Bulletin of the American Physical Society 43(1), 24 (March, 1998).
- I. P. Herman, "Optical Probing of Surfaces During Etching, Chemical Structure and Dynamics Seminar," William R. Wiley Environmental Molecular Sciences Laboratory, Battelle Pacific Northwest National Laboratory, July 23, 1998.

- I. P. Herman, invited, "Optical Probing of Surfaces during Plasma Etching and Other Thin Film Processes," Optical Diagnostics for Thin Film Processing Session, Rocky Mountain American Vacuum Society Symposium 1998, August 20, 1998.
- I. P. Herman, "Infrared Reflection Spectroscopy of As-Anodized and Passivated 6H and 4H Porous Silicon Carbide," International Conference on Porous Semiconductors Science and Technology, Mallorca, Abstract O-44, Spain, March 16-20, 1998, with J. E. Spanier.
- J. E. Spanier and I. P. Herman "Mean-Field Dielectric Function Modeling of Porous Silicon Carbide using a Statistical Approach," Materials Research Society Fall Meeting, Presentation F5.32, Boston, November 30 -December 4, 1998.
- I. P. Herman, "Optical Probes of Semiconductor Surfaces During Etching," Department of Materials Engineering Seminar, Technion - Israel Institute of Technology, January 14, 1999.
- I. P. Herman, "Optical Probes of Semiconductor Surfaces During Plasma Etching," Physical Chemistry Seminar, Hebrew University, Jerusalem, Israel, January 11, 1999.
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INVENTIONS

None

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